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CRYSTALLIZATION AND LUMINESCENCE PROPERTIES OF $(\text{Sm}_x\text{Y}_{1-x})_2\text{O}_3\text{--Al}_2\text{O}_3\text{--B}_2\text{O}_3$ GLASS

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Glass and products of solid-phase synthesis in the form of samarium-activated single-phase powders with huntite structure were obtained in the system $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3\text{--B}_2\text{O}_3$. It was shown that the glasses studied crystallize with predominately aluminum borate $\text{Al}_3\text{B}_2\text{O}_9$ precipitating in the bulk and the solid solution $(\text{Y, Sm})\text{Al}_3(\text{BO}_3)_4$ on the surface of the sample. When the crystalline powders $(\text{Sm}_x\text{Y}_{1-x})\text{Al}_3(\text{BO}_3)_4$ transitioned into an amorphous state leveling of the Stark structure and broadening of the luminescence bands of Sm^{3+} was observed, but the luminescence branching ratios changed very little. It was found that lowering the synthesis temperature of such glasses from 1450 to 1250°C increases the BO_4 fraction and quantum yield of luminescence with low activator concentration.

Key words: aluminum-borate glasses, $\text{YAl}_3(\text{BO}_3)_4$, crystallization of glasses, luminescence properties of samarium.

Glasses activated by rare-earth ions are used as active media for different types of solid-state lasers and amplifiers. Many laser rare-earth ions are characterized by concentration self-quenching of luminescence, owing mainly to cross-relaxation processes [1]. Such self-quenching is most strongly expressed in quartz glasses, for which segregation of the rare-earth activator is characteristic [2] because of the large difference in the coordination number of the latter and the silicon ions. For multicomponent glasses concentration luminescence quenching processes are much weaker.

However, literally only isolated glass compositions giving a quite isolated position of the rare-earth activators are currently known. The best known impurity is Li–Ln phosphate glass, for which the shortest Ln–Ln distance is 5.6 Å [3]. The relatively large value of this parameter is one of the most important reasons for the anomalously weak concentration quenching of the luminescence of Ln^{3+} in this glass.

It has been shown in a spectral-luminescence study of the system $(\text{Sm}_x\text{Y}_{1-x})_2\text{O}_3\text{--Al}_2\text{O}_3\text{--B}_2\text{O}_3$ with composition close to huntite $\text{CaMg}_3(\text{CO}_3)_4$ stoichiometry that for them the shortest Ln–Ln distance is even larger — 6.5 Å. This makes $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3\text{--B}_2\text{O}_3$ (YAB) glasses promising matrices for ac-

tivation by rare-earth ions with relatively efficient cross-relaxation quenching of luminescence.

It should be noted that glass formation in the system YAB has not been adequately studied. Specifically, a small composition range bordering on the composition of the huntite-like crystal $\text{YAl}_3(\text{BO}_3)_4$, in which transparent glasses can be obtained, was determined in [6]. The authors of [7] obtained uniform glasses with B_2O_3 molar content⁴ from 50 to 65%. The density, refractive index and linear thermal expansion coefficient (CLTE) of such glasses increase when yttrium oxide is substituted for B_2O_3 or Al_2O_3 . In addition, the glass-formation temperature t_g of glasses with composition close to that of a huntite-like crystal is high — $t_g > 700^\circ\text{C}$ [7]. It is shown in [8] that the glass formation region in the YAB system can be enlarged by using technologically barely acceptable glassmaking conditions — 1800°C in a nitrogen atmosphere. The luminescence properties of YAB glasses activated by rare-earth ions are also poorly described; only several works study glasses with Eu^{3+} [9] and Nd^{3+} [8] ions, but there is no information on the effect of the synthesis temperature on their properties. At the same time as this temperature increases the equilibrium between the molecular groupings BO_4 and BO_3 is displaced in the direction of the latter [10]. Since the BO_3 groupings are characterized by higher stretching vibration frequencies compared with BO_4 ($\nu \sim 1300\text{ cm}^{-1}$ as opposed to about 1100 cm^{-1} [9]), increasing

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⁴ Here and below, the molar content.

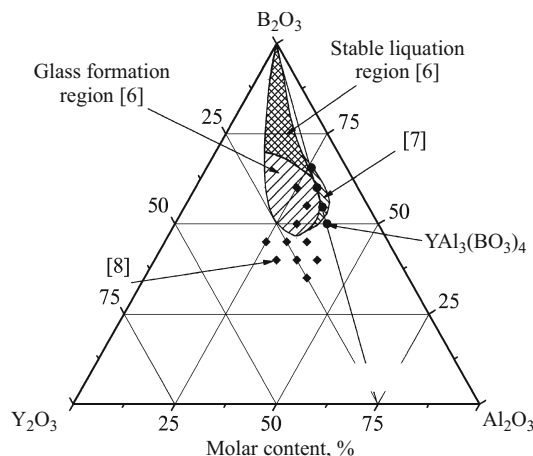


Fig. 1. Region of glass formation in the system $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ using data from [6–8]: ● compositions along the line $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3 = 1/3$, studied in the present work.

their fraction can have a negative effect on the quantum yield of luminescence of the activators with a small energy gap between the metastable and closest lower-lying levels.

On this basis the present article studies the crystallization of YAB glasses and investigates the effect of their synthesis temperature on the luminescence properties. Sm^{3+} ions were chosen as activators; they have no induced absorption from a metastable state and are promising for creating media lasing at $\lambda \approx 600$ and 650 nm.

EXPERIMENTAL PROCEDURE

The following were synthesized: glasses with the compositions (%) $12.5(\text{Sm}_x\text{Y}_{1-x})_2\text{O}_3$, $37.5\text{Al}_2\text{O}_3$ and $50.0\text{B}_2\text{O}_3$ ($x = 0.1 - 4\%$) and powders of huntite-like polycrystals $(\text{Sm}, \text{Y})\text{Al}_3(\text{BO}_3)_4$ with the same compositions as well as glasses with higher B_2O_3 content in the glass-formation region (Fig. 1). Ultrapure Sm_2O_3 , Y_2O_3 , $\text{Al}(\text{OH})_3$ and H_3BO_3 were used as the initial components for glassmaking and solid-phase synthesis. Melting was done in platinum crucibles at temperature $T_{\text{syn}} = 1250 - 1550^\circ\text{C}$ for 1 h depending on the composition and amount of glass. The melt was poured onto a metal plate and another plate was used to press the melt to thickness about 2–3 mm. Solid-phase synthesis of huntite-like polycrystals was done in corundum crucibles at 1160°C for 4.5 h.

A DRON 3M diffractometer ($\text{CuK}\alpha$ radiation, Ni filter) was used for x-ray phase analysis (XPA) of the samples and products of crystallization of glasses obtained in subsequent heat-treatments. All glasses were also investigated by differential thermal analysis (DTA) with heating rate 10 K/min and by differential scanning calorimetry (DSC) with a Netzsch STA 449F3 simultaneous high-temperature thermal analyzer.

The absorption spectra were recorded with a Cary 500 spectrophotometer and the luminescence spectra with a

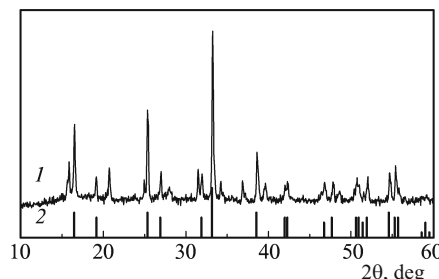


Fig. 2. Diffraction patterns of $\text{SmAl}_3(\text{BO}_3)_4$ polycrystals (1) obtained by solid-phase synthesis and JCPDS 18-0058 line diffraction pattern (2).

SDL-2 spectrofluorimeter. The latter spectra were corrected for the spectral sensitivity of the detection system and represented curves of the number of quanta per unit wavelength $dN/d\lambda$ versus λ . The combination scattering spectra were recorded with a Spectra Pro-500i RS spectrometer at 180° with $\lambda = 532$ nm laser excitation. A S9–8 digital oscillograph with excitation of the second harmonic of a single-pulse sapphire with titanium laser ($\lambda = 402$ nm, pulse duration at half-height about 10 nsec) was used to study the luminescence decay kinetics.

EXPERIMENTAL RESULTS AND DISCUSSION

According to XPA the powders obtained by solid-phase synthesis contained only the huntite-like $\text{YAl}_3(\text{BO}_3)_4$ and $\text{SmAl}_3(\text{BO}_3)_4$ crystals (see, for example, JCPDS card No. 18-0058) or their solid solutions (Fig. 2). Because of the small difference of the lattice parameters it was very difficult to distinguish the solid solution and individual phases under the conditions chosen for the x-ray diffraction experiment. All synthesized glasses are x-ray amorphous and their diffraction patterns are practically identical to that of glass with 0.3% Sm_2O_3 (Fig. 3, curve 1).

Three exothermal peaks are seen in the DTA curves of glass powders with huntite composition $12.5(\text{Sm}_x\text{Y}_{1-x})_2\text{O}_3$, $37.5\text{Al}_2\text{O}_3$, and $50.0\text{B}_2\text{O}_3$ (Fig. 4). As the B_2O_3 concentration increases the second photoeffect almost vanished (Fig. 5), which, evidently, is due to a decrease of the crystallizability of the glass. Crystallization of all the glasses studied starts at temperatures above 800°C . According to XPA (Fig. 3, curves 2–5) its products are: aluminum borate $\text{Al}_4\text{B}_2\text{O}_9$ (JCPDS No. 29-0010), yttrium borate YBO_3 and samarium SmBO_3 (JCPDS Nos. 13-0479 and 16-0277, respectively) as well as the huntite-like phases $\text{YAl}_3(\text{BO}_3)_4$ and $\text{SmAl}_3(\text{BO}_3)_4$ (JCPDS Nos. 72-1978 and 18-0058, respectively) or their solid solutions. When glasses were heat-treated in the region of the first crystallization peak the main crystallized phase was aluminum borate. As the Sm_2O_3 content increases from 0.3 to 4% the exothermal peaks shift to lower temperatures and the glass formation temperature and intensity of the second exothermal effect on the DTA curve decrease (Fig. 4).

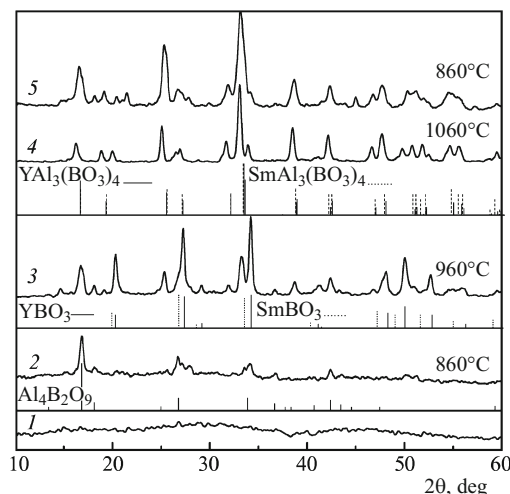


Fig. 3. Powder diffraction pattern of glass with molar content (%): 0.3Sm₂O₃, 12.2Y₂O₃, 37.5Al₂O₃ and 50.0B₂O₃: 1) initial glass; 2) monolithic sample, heat-treated for 3 h at 860°C; 3) same, heat-treated at 960°C; 4) same at 1060°C; 5) comminuted sample, heat-treated for 3 h at 860°C.

At the temperature of the second exothermal peak the glasses crystallize with mainly yttrium borate and samarium being released. As the Sm₂O₃ content increases concurrent release of the borates indicated above occurs, as a result of which the glasses are less prone to crystallization on heating and in consequence the intensity of the second exo effect on the DTA curve decreases. When all of the experimental glasses are heat-treated near the third exothermal peak the crystallization of predominantly the huntite-like phases is observed.

Comparing the DSC curves of monolithic and powder samples of the experimental systems (Fig. 5) it can be concluded that volume crystallization occurs at temperatures close to the temperature of the first exothermal peak. It is known that DSC in the uniform heating regime makes it possible to determine the effect of the surface on the crystallization processes occurring in glass [11]. The larger the total number of embryos formed in the interior and on the surface of the glass at a prescribed heating rate, the lower the temperature of the exothermal peak on the DSC curve is [12]. The presence of a distinct exothermal peak on the DSC curve of monolithic samples (Fig. 5, curves 1 and 3) suggests that volume crystallization very likely exists. In addition, the first exo effect, which is associated with the precipitation of aluminum borate Al₄B₂O₉, hardly shifts at all in the direction of low temperatures as the sample is comminuted (Fig. 5, curves 2 and 4).

In contrast to this, the high temperature exo effect due to the precipitation of huntite-like crystals shifts in the direction of low temperatures as the sample is comminuted. This attests to surface crystallization near 1050°C.

Analysis of the diffraction patterns of heat-treated glass samples (powdered or monolithic; see Fig. 3, curves 2 and 5) confirms the conclusion drawn. Evidently, the diffraction

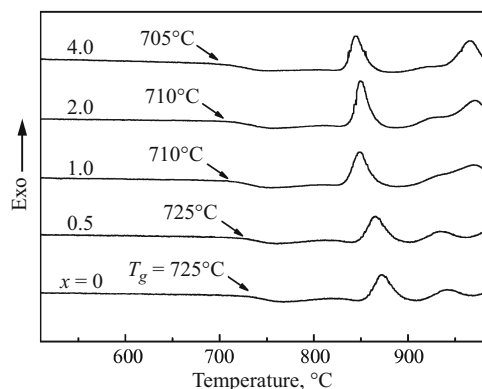


Fig. 4. DTA curves of glass powders with molar content (%): xSm₂O₃, (12.5 - x)Y₂O₃, 37.5Al₂O₃, and 50.0B₂O₃, where x = 0 - 4% (indicated on the curves).

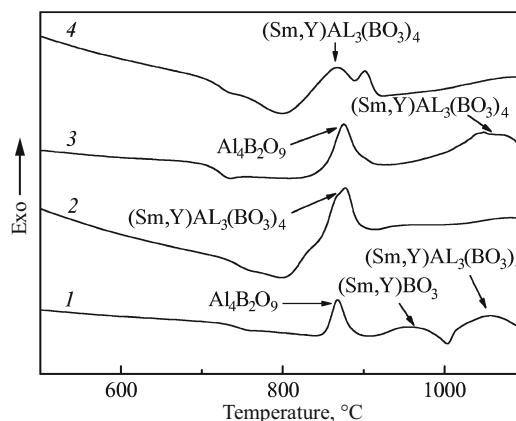


Fig. 5. DSC curves of monolithic (1, 3) and powdered (2, 4) glass samples with molar content (%): 1, 2) 0.3Sm₂O₃, 12Y₂O₃, 37.5Al₂O₃, and 50.0 B₂O₃; 3, 4) 0.3Sm₂O₃, 9.7Y₂O₃, 30Al₂O₃, and 60B₂O₃.

patterns obtained for powdered and monolithic glass with same composition and under identical conditions of heat treatment (860°C, 3 h) differ strongly. Increasing the specific surface area by comminution increases the amount of the huntite-like phase crystallized from the surface (see Fig. 3, curve 5). The diffraction patterns of powder obtained by comminution of heat-treated monolithic sample attests to the presence of another phase — aluminum borate, which successively precipitates in the interior of the glass (see Fig. 3, curve 2).

Increasing the B₂O₃ content greatly lowers t_{syn} . For example, $t_{\text{syn}} = 1470^\circ\text{C}$ for the glass 0.3Sm₂O₃, 9.7Y₂O₃, 30Al₂O₃, and 60B₂O₃; this is 70°C lower than for glass with huntite-like crystal composition. Lowering t_{syn} decreases the amount of atomic platinum dissolved in the glass, facilitates mixing and creates favorable conditions for obtaining optical-quality parts. As the B₂O₃ content increases the glass-forming capacity of melt improves while the glass is less likely to crystallize on heating. It is known that the propensity of glass to-

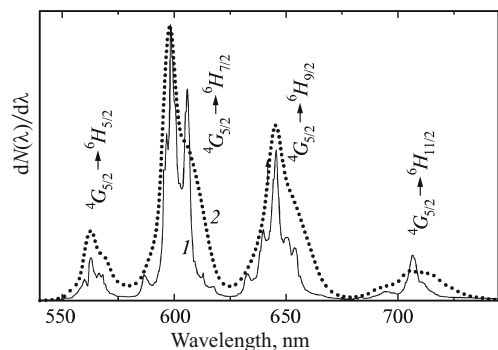


Fig. 6. Luminescence spectra of huntite-like polycrystal (1) and glass (2) containing 1% Sm_2O_3 ($\lambda_{\text{exc}} = 402$ nm).

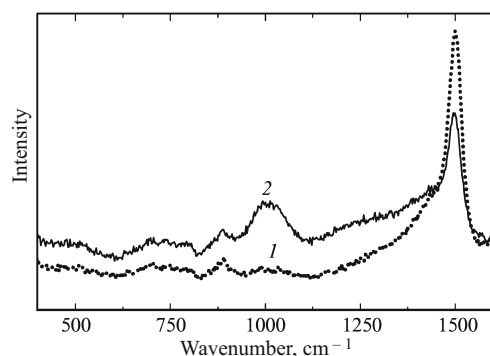


Fig. 7. Raman scattering spectra of glasses with molar content (%): $2\text{La}_2\text{O}_3$, $13\text{Y}_2\text{O}_3$, $15\text{Al}_2\text{O}_3$, and $70\text{B}_2\text{O}_3$ synthesized at 1450°C (1) and 1250°C (2).

ward crystallization is inversely proportional to the difference between the temperature t_{c1} of the first exothermal effect and the glass-formation temperature t_g [13]. This difference was 170°C for glass with the composition $0.3\text{Sm}_2\text{O}_3$, $9.7\text{Y}_2\text{O}_3$, $30\text{Al}_2\text{O}_3$, and $60\text{B}_2\text{O}_3$ and 140°C for $0.3\text{Sm}_2\text{O}_3$, $12.2\text{Y}_2\text{O}_3$, $37.5\text{Al}_2\text{O}_3$, and $50\text{B}_2\text{O}_3$, which is probably because the B_2O_3 content is lower in the second glass.

The luminescence spectra of huntite-like polycrystals and glasses consist of a series of relatively narrow bands due to transitions from the metastable state $^4G_{5/2}$ of Sm^{3+} ions (Fig. 6). The fraction of the quanta emitted from this state in longer-wavelength transitions is about 20% (not shown in Fig. 6). On switching from a polycrystalline to a glass matrix the Stark structure of the bands is leveled and the bands undergo considerable broadening. The branching ratios of the luminescence defined as the ratio of the fraction of quanta in an individual band to the total number of quanta emitted from the state $^4G_{5/2}$ are approximately conserved. No changes are observed when the Sm_2O_3 concentration or the wavelength is varied; this is indicative of high uniformity of the optical centers. Such changes are likewise practically absent as the B_2O_3 content increases and t_{syn} changes.

As shown in [4], the maximum quantum yield of luminescence of Sm^{3+} ions in such glasses is bounded by the 80%

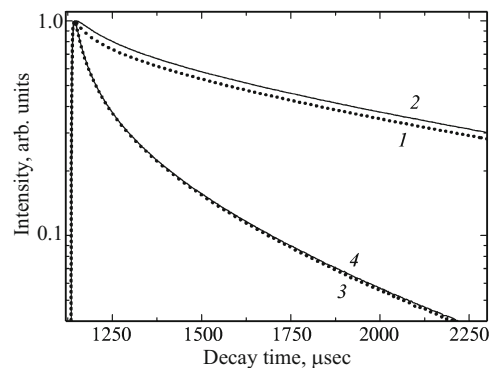


Fig. 8. Luminescence decay kinetics of Sm^{3+} ions in glasses with molar content (%): $0.5\text{Sm}_2\text{O}_3$, $14.5\text{Y}_2\text{O}_3$, $15\text{Al}_2\text{O}_3$, $70\text{B}_2\text{O}$ (1, 2) and $2\text{Sm}_2\text{O}_3$, $13\text{Y}_2\text{O}_3$, $15\text{Al}_2\text{O}_3$, $70\text{B}_2\text{O}_3$ (3, 4), $t_{\text{syn}} = 1450$ (1, 3) and 1250°C (2, 4) ($\lambda_{\text{exc}} = 402$ nm, $\lambda_{\text{det}} = 598$ nm).

level because of intra-center nonradiative excitation transfer to vibrations of glass-forming groups BO_3 . For this reason it was of interest to determine the possibility of increasing this yield by decreasing the fraction of the indicated groups, which can be accomplished by lowering t_{syn} .

Glass with the composition $15(\text{Ln}_x\text{Y}_{1-x})_2\text{O}_3$, $15\text{Al}_2\text{O}_3$, and $17\text{B}_2\text{O}_3$ was chosen for this; it can be synthesized in a wide temperature range. Analysis of its Raman scattering spectra (Fig. 7), performed to eliminate luminescence on La-containing glass, shows that when t_{syn} is lowered from 1450 to 1250°C the intensity of the wide diffusion band at $\nu \approx 1000\text{ cm}^{-1}$ increases many-fold and the band at $\nu \approx 1500\text{ cm}^{-1}$ weakens considerably at the same time. According to [14] these bands are due to stretching vibrations of B–O–B bridges in BO_4 groupings (low-frequency) and vibration of B–O $^-$ bonds in chains and rings of metaborates (high-frequency), i.e., the BO_4 fraction increases.

It is natural to expect that such structural reorganization of the matrix must be reflected in the decay rate of the metastable state of the Sm^{3+} ions. The luminescence decay kinetics of glasses with the following compositions was studied: $0.5\text{Sm}_2\text{O}_3$, $14.5\text{Y}_2\text{O}_3$, $15\text{Al}_2\text{O}_3$, and $70\text{B}_2\text{O}$ (curves 1 and 2) and $2\text{Sm}_2\text{O}_3$, $13\text{Y}_2\text{O}_3$, $15\text{Al}_2\text{O}_3$, and $70\text{B}_2\text{O}_3$ (curves 3 and 4); the synthesis temperatures were 1450°C (curves 1 and 3) and 1250°C (curves 2 and 4). It is evident that when t_{syn} is lowered the decay rate of decreases considerably with low activator concentration and has virtually no effect on this rate at high concentration. The average luminescence decay time, defined as $\bar{\tau} = I_{\text{max}}^{-1} \int I(t) dt$, where I is the luminescence intensity, was $1060\text{ }\mu\text{sec}$ for curve 1 and $1150\text{ }\mu\text{sec}$ for curve 2.

Taking account of the absence of any changes in the absorption and luminescence spectra of these glasses, which indicate a t_{syn} dependence of the radiative decay time of the metastable state of the Sm^{3+} ions, the observed 8% increase of $\bar{\tau}$ and therefore of the quantum yield can be attributed to the weakening of the multi-photon relaxation between the

states $^4G_{5/2}$ and $^6F_{11/2}$. For highly doped glass this weakening becomes unnoticeable against the background of the effective quenching of luminescence by the cross-relaxation mechanism.

It should be noted that glasses synthesized in air are characterized by an appreciable content of OH^- groups — the peak linear absorption coefficient in the region of their fundamental stretching bands at $\nu \sim 3460 \text{ cm}^{-1}$ ($\lambda \approx 2890 \text{ nm}$) is $4 - 9 \text{ cm}^{-1}$. These groups can be quite effective quenchers of luminescence if the energy gaps between the metastable and closest lower-lying states of the activator are relatively wide ($\Delta E > 4000 - 5000 \text{ cm}^{-1}$). For Sm^{3+} ions this gap width is about 7500 cm^{-1} , which is only 2.2 times greater than the vibration quantum of this impurity oscillator. For this reason, it would be desirable to remove water from Sm-containing glasses intended for the manufacture of active elements, especially if OH^- groups enter into the immediate environment of the activator ion. One technological method of such water removal is bubbling oxygen through melt. It turned out that bubbling for 30 min for $0.3\text{Sm}_2\text{O}_3$, $9.7\text{Y}_2\text{O}_3$, $30\text{Al}_2\text{O}_3$, and $60\text{B}_2\text{O}_3$ glass decreases the concentration of OH^- groups by approximately 30% with no change in the luminescence spectrum. It is noteworthy that even the removal of such a small amount of water increased the intensity of the luminescence of this glass by approximately 20%. However, the kinetic curves of luminescence decay hardly changed, which leaves unanswered the question of why the observed increase occurs.

In summary, $(\text{Sm}_x\text{Y}_{1-x})_2\text{O}_3\text{--Al}_2\text{O}_3\text{--B}_2\text{O}_3$ glasses crystallize with precipitation of aluminum borate $\text{Al}_4\text{B}_2\text{O}_9$ in the interior and the solid solution $(\text{Y, Sm})\text{Al}_3(\text{BO}_3)_4$ on the surface of the sample. Increasing their B_2O_3 content from 50 to 60% decreases the synthesis temperature from 1540 to 1470°C and is accompanied by proneness toward crystallization, which is good for obtaining optical-quality glass; the introduction of 70% B_2O_3 makes it possible to synthesize glass at 1250°C also. For the experimental glasses the luminescence branching ratios for Sm^{3+} ions are close to the corresponding values of the huntite-like powders $(\text{Sm}_x\text{Y}_{1-x})\text{Al}_3(\text{BO}_3)_4$. For low activator concentration decreasing the synthesis temperature of such glasses from 1450 to 1250°C results in high BO_4 concentration and quantum yield of luminescence. The latter can also be increased by removing water from the glass by bubbling oxygen through the melt.

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